

Effect of Elastic Constants on the Ultrasonic Properties of Group VIB Transition Metal Diborides

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Abstract: The ultrasonic properties like ultrasonic attenuation, sound velocity in the group VIB transition metal diborides like CrB₂ and MoB₂ have been studied along unique axis at room temperature. The second- and third order elastic constants (SOEC & TOEC) have been calculated for these diborides using Lennard–Jones potential. The velocities V_L and V_{S2} increases with the angle from the unique axis and V_{S1} have maximum at 45° with unique axis of the crystal. The inconsistent behaviour of angle dependent velocities is associated to the action of second order elastic constants. Debye average sound velocities of these compounds are increasing with the angle and has maximum at 55° with unique axis at room temperature. Hence when a sound wave travels at 55° with unique axis of these materials, then the average sound velocity is found to be maximum. The mechanical properties of CrB₂ are better than MoB₂, because CrB₂ has low ultrasonic attenuation comparison than MoB₂. The comparison of calculated ultrasonic parameters with available theoretical/experimental physical parameters gives information about classification of these compounds.

Keywords: Elastic properties, transition metal diborides, thermal conductivity, ultrasonic properties.

1. INTRODUCTION

Borides of transition metals have various unique properties which in many cases are of great importance from technological view points. Among their attractive properties are high thermal and chemical stability, high electrical and thermal conductivity, and high hardness and high mechanical stiffness [1]. VIB transition metal diborides, CrB₂ and MoB₂ with the hexagonal structure (space group: p6/mmm) exhibit a wide variety of attractive properties and thus may attract for a long time much attention of physicists and material scientists due to their unique physical and chemical properties such as hardness, high melting points, chemical inertness, etc. and belong to the most promising engineering materials with a wide range of industrial applications [2-4]. Grechnev et al. [5] have studied as effect of pressure on the magnetic properties of CrB₂ and Okada et al. [6] have investigated crystal structure and thermal properties of MoB₂.

Ultrasonic offer the possibility to detect and characterize microstructural properties as well as flaws in materials, controlling materials behaviour based on physical mechanism to predict future performance of the materials. Various investigators have shown considerable interest on ultrasonic properties of metals and alloys. Wave propagation velocity is key parameter in ultrasonic characterization and can provide information about crystallographic texture. The ultrasonic velocity is directly related to the elastic constants by the relationship $V = \sqrt{C/\rho}$, where 'C' is the relevant elastic constants and 'ρ' is the density of that particular material. Also ultrasonic attenuation

is very important physical parameter to characterize the material, which is well related to several physical quantities like thermal conductivity, specific heat, thermal energy density and higher order elastic constants [7, 8]. The elastic constants provide valuable information about the bonding characteristic between adjacent atomic planes and the anisotropic character of the bonding and structural stability [9, 10].

Therefore, in this work we predict the ultrasonic properties of hexagonal structured CrB₂ and MoB₂ at room temperature. The ultrasonic attenuation coefficient, acoustic coupling constants, higher order elastic constants, thermal relaxation time and ultrasonic wave velocities for these diborides for each direction of propagation of wave are calculated at room temperature.

The calculated ultrasonic parameters are discussed with related thermophysical properties for the characterization of the chosen metals. The obtained results are analyzed in comparison to other hexagonal structured materials.

2. THEORY

In the present investigation, the theory is divided into two parts:

2.1 Second and third order elastic constants

The second (C_{IJ}) and third (C_{IJK}) order elastic constants of material are defined by following expressions.

$$C_{IJ} = \frac{\partial^2 U}{\partial e_I \partial e_J}; \quad I \text{ or } J = 1, \dots, 6 \quad (1)$$

$$C_{IJK} = \frac{\partial^3 U}{\partial e_I \partial e_J \partial e_K}; \quad I \text{ or } J \text{ or } K = 1, \dots, 6 \quad (2)$$

where, U is elastic energy density, $e_i = e_{ij}$ (i or j = x, y, z, I=1, ...6) is component of strain tensor. Equations (1) and (2) leads six second and ten third order elastic constants (SOEC and TOEC) for the hexagonal close packed structure materials [7, 11].

$$\left. \begin{aligned} C_{11} &= 24.1 p^4 C' & C_{12} &= 5.918 p^4 C' \\ C_{13} &= 1.925 p^6 C' & C_{33} &= 3.464 p^8 C' \\ C_{44} &= 2.309 p^4 C' & C_{66} &= 9.851 p^4 C' \end{aligned} \right\} \quad (3a)$$

$$\left. \begin{aligned} C_{111} &= 126.9 p^2 B + 8.853 p^4 C' & C_{112} &= 19.168 p^2 B - 1.61 p^4 C' \\ C_{113} &= 1.924 p^4 B + 1.155 p^6 C' & C_{123} &= 1.617 p^4 B - 1.155 p^6 C' \\ C_{133} &= 3.695 p^6 B & C_{155} &= 1.539 p^4 B \\ C_{144} &= 2.309 p^4 B & C_{344} &= 3.464 p^6 B \\ C_{222} &= 101.039 p^2 B + 9.007 p^4 C' & C_{333} &= 5.196 p^8 B \end{aligned} \right\} \quad (3b)$$

where $p = c/a$: axial ratio; $C' = \chi a^3 / p^5$; $B = \psi a^3 / p^3$; $\chi = (1/8)[\{nb_0(n-m)\} / \{a^{n+4}\}]$

$\psi = -\chi / \{6 a^2 (m+n+6)\}$; m, n=integer quantity; b_0 =Lennard Jones parameter.

2.2 Ultrasonic attenuation and allied parameters

The predominant causes for the ultrasonic attenuation in a solid at room temperature are phonon-phonon interaction (Akhieser loss) and thermoelastic relaxation mechanisms. The ultrasonic attenuation coefficient $(A)_{\text{Akh}}$ due to phonon-phonon interaction and thermoelastic relaxation mechanisms is given by the following expression [11, 12].

$$(A/f^2)_{\text{Akh}} = 4\pi^2 \left(3E_0 \langle (\gamma_i^j)^2 \rangle - \langle \gamma_i^j \rangle^2 C_V T \right) \tau / 2\rho V^3 \quad (4)$$

$$(A/f^2)_{\text{Th}} = 4\pi^2 \langle \gamma_i^j \rangle^2 kT / 2\rho V_L^5 \quad (5)$$

where, f: frequency of the ultrasonic wave; V: ultrasonic velocity for longitudinal and shear wave; V_L : longitudinal ultrasonic velocity; E_0 : thermal energy density; γ_i^j : Grüneisen number (i, j are the mode and direction of propagation).

The Grüneisen number for hexagonal structured crystal along $\langle 001 \rangle$ orientation or $\theta=0^\circ$ is direct consequence of second and third order elastic constants.

$D = 3(3E_0 \langle (\gamma_i^j)^2 \rangle - \langle \gamma_i^j \rangle^2 C_V T) / E_0$ is known as acoustic coupling constant, which is the measure of acoustic energy converted to thermal energy. When the ultrasonic wave propagates through crystalline material, the equilibrium of phonon distribution is disturbed. The time for re-establishment of equilibrium of the thermal phonon distribution is called thermal relaxation time (τ) and is given by following expression:

$$\tau = \tau_s = \tau_L / 2 = 3k / C_V V_D^2 \quad (6)$$

Here τ_L and τ_s are the thermal relaxation time for longitudinal and shear wave. k and C_V are the thermal conductivity and specific heat per unit volume of the material respectively. The Debye average velocity (V_D) is well related to longitudinal (V_L) and shear wave (V_{S1}, V_{S2}) velocities. The expressions for ultrasonic velocities are given in our previous paper [12]. Where ρ and θ are the density of the material and angle with the unique axis of the crystal respectively. The ultrasonic velocities have been used for the calculation of ultrasonic attenuation and allied parameters in the chosen materials.

3. RESULTS & DISCUSSION

3.1 Higher order elastic constants

The unit cell parameters 'a' (basal plane parameter) and 'p' (axial ratio) for CrB_2 and MoB_2 are 2.973Å, 3.000Å and 1.033, 1.107 respectively [13, 14]. The value of m and n for chosen materials are 6 and 7. The values of b_0 are 2.0×10^{-64} erg cm^7 and 2.4×10^{-64} erg cm^7 for CrB_2 and MoB_2 respectively. The SOEC and TOEC have been calculated for these compounds using equation. (3) and are presented in Table 1.

Table 1. Second and third order elastic constants (SOEC and TOEC) & Bulk Modulus (B) in the unit of GPa of CrB_2 and MoB_2 compounds at room temperature.

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B
CrB_2	545.6	133.9	99.5	330.7	107.3	213.9	233
MoB_2	609.2	149.5	196.3	393.3	155.5	248.8	305.4
[15] CrB_2	583.7	117.3	119.7	343.3	141.1	233.2	247.1
[14] MoB_2	627.0	120.0	231.0	398.0	174.0	253.5	313.0

	C_{111}	C_{112}	C_{113}	C_{123}	C_{133}	C_{344}	C_{144}	C_{155}	C_{222}	C_{333}
CrB_2	-8896	-1410	-229	-291	-1117	-1047	-339	-227	-7039	-3225
MoB_2	-9933	-1575	-247	-314	-1159	-1087	-366	-244	-7860	-3227

The calculated SOEC are slightly smaller than the experimental/ theoretically method [14, 15]. Actually Okamoto et al [15] has based the X-ray back reflection Lau method and Chen et al [14] has based on the density functional theory. Although obtained SOEC are of the same order as others [14, 15]. Which are in good agreement with theoretical and experimental results as shown in Table 1. The obtained values of the SOEC and TOEC are of the same order as previous experimental and theoretical studies of diborides compounds [16, 17]. Hence our theoretical approach to evaluate elastic constants seems to valid for compounds. The bulk modulus (B) for these compounds can be calculated with the formula $B = \frac{2(C_{11} + C_{12} + 2C_{13} + C_{33}/2)}{9}$. The evaluated B for these materials is presented in Table 1.

3.2 Ultrasonic velocity and allied parameters

The density and thermal conductivity at room temperature have been taken from the literature [13, 14]. The value of C_V and E_0 are evaluated using tables of physical constants and Debye temperature. The quantities ρ , C_V , E_0 , k and calculated acoustic coupling constants (D_L & D_S) are presented in Table 2.

Table 2: Density (ρ : in 10^3 kg m^{-3}), specific heat per unit volume (C_V : in $10^6 \text{ Jm}^{-3} \text{ K}^{-1}$), thermal energy density (E_0 : in 10^8 Jm^{-3}), thermal conductivity (k : in $\text{Wm}^{-1} \text{ K}^{-1}$) and acoustic coupling constant (D_L , D_S) of CrB_2 and MoB_2 compounds.

Compounds	ρ	C_V	E_0	k	D_L	D_S
CrB_2	5.18	1.40	2.13	26.0	35.42	3.90
MoB_2	7.78	1.41	2.36	16.3	30.65	2.89

The calculated orientation dependent ultrasonic wave velocities and Debye average velocities at 300 K are shown in Figures 1–4. Figures 1–3 show that the V_L and V_{S2} increases with the angle from the unique axis and V_{S1} have maximum at 45° with unique axis of the crystal. The combined effect of SOEC and density is reason for abnormal behaviour of angle dependent velocities.

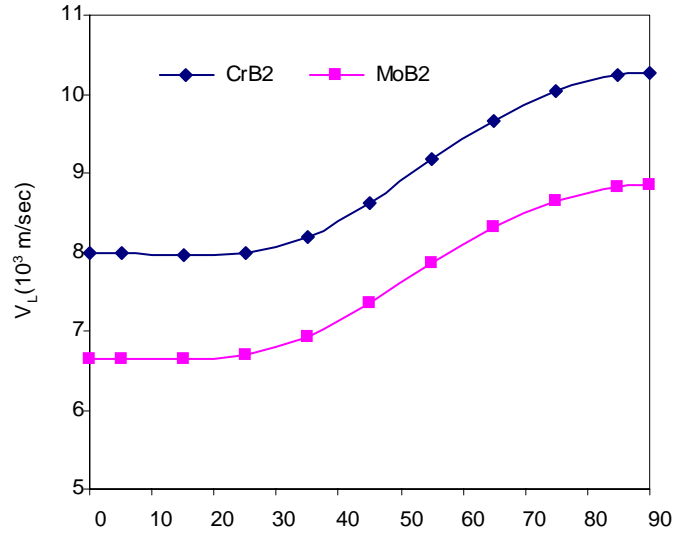


Figure 1. V_L vs angle with unique axis of crystal

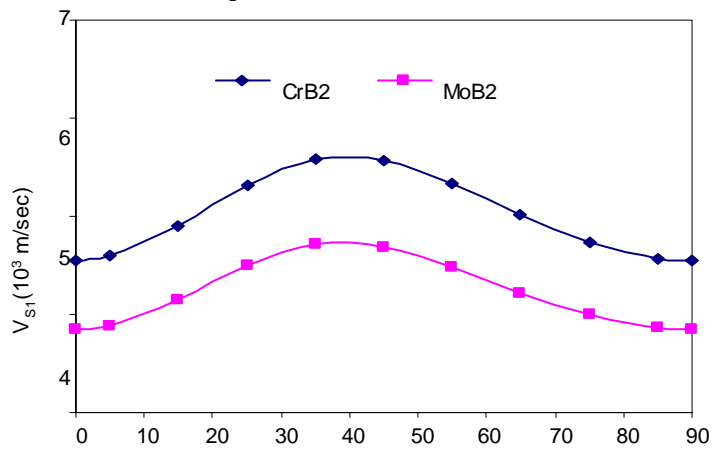


Figure 2. V_{S1} vs angle with unique axis of crystal

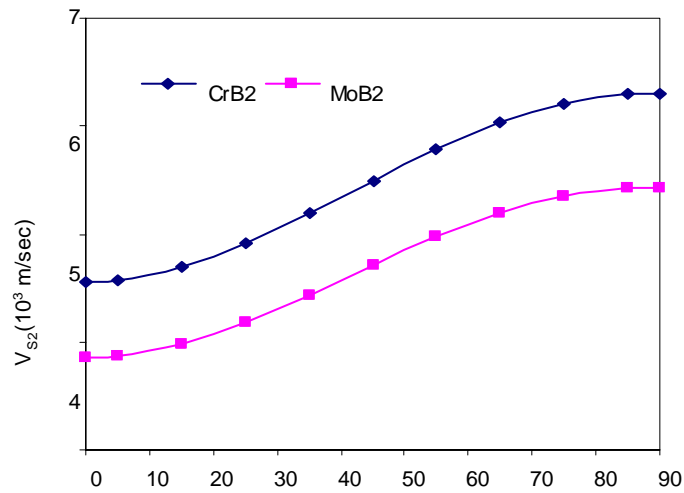


Figure 3. V_{S2} vs angle with unique axis of crystal

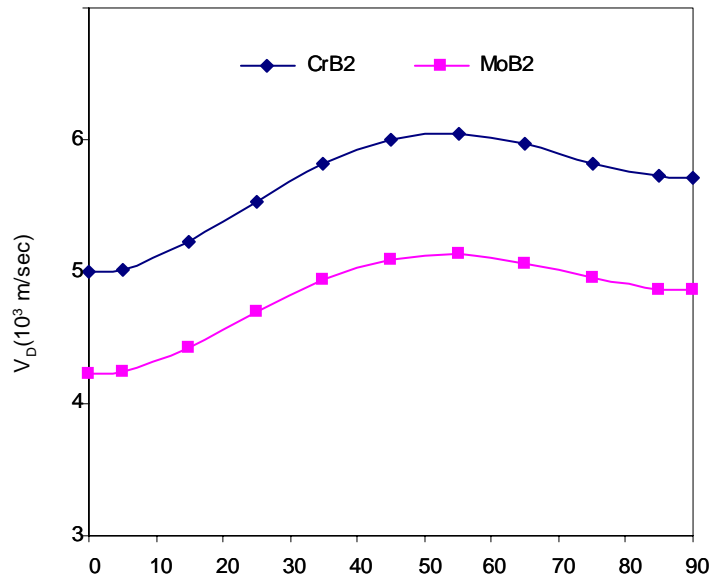


Figure 4. V_D vs angle with unique axis of crystal

The nature of the angle dependent velocity curves in the present work is found similar as that for heavy rare-earth metals, laves-phase compounds, lanthanides metals and other hexagonal wurtzite structured materials (GaN, AlN, InN) [17-21]. Thus the computed velocities for these materials are justified.

Debye average velocities (V_D) of these compounds are increasing with the angle and have maxima at 55° at 300 K (Figure 4). Since V_D is calculated using V_L , V_{S1} and V_{S2} [17, 20], therefore the angle variation of V_D is influenced by the constituent ultrasonic velocities. The maximum V_D at 55° is due to a significant increase in longitudinal and pure shear (V_{S2}) wave velocities and a decrease in quasi-shear (V_{S1}) wave velocity. Thus it can be concluded that when a sound wave travels at 55° with the unique axis of these materials then the average sound wave velocity is maximum.

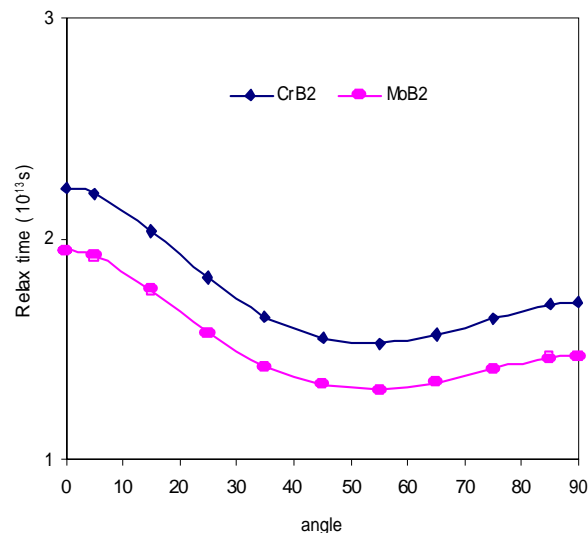


Figure 5. Relaxation time vs angle with unique axis of crystal

The thermal relaxation time for hexagonal structured material follows the equation

$\tau = \tau_0 \exp(x/\lambda)$, where τ and λ are constants. The order of ‘ τ ’ for hexagonal structure is in picoseconds [20]. With reference some previous work [21, 22], the size dependency of τ for bcc and fcc structured materials follow the equation $\tau = \tau_0 [1 - \exp(-x/\lambda)]$. Thus it can be said that the thermal relaxation time is not only function of size and temperature but also depends on the structure of a materials. Hence the calculated τ justifies the hcp structure of chosen compounds at room temperature. The minimum τ for wave propagation along $\theta = 55^\circ$ implies that the re-establishment time for the equilibrium distribution of thermal phonons will be minimum for propagation of wave along this direction. Thus the present average sound velocity directly correlates with the Debye temperature, specific heat and thermal energy density of these materials.

3.3 Ultrasonic attenuation

In the evaluation of ultrasonic attenuation, it is supposed that wave is propagating along the unique axis (<001> direction) of these metals. The attenuation coefficient over frequency square $(A/f^2)_{\text{Akh}}$ for longitudinal $(A/f^2)_L$ and shear wave $(A/f^2)_S$ are calculated using Equation (4) under the condition $\omega\tau \ll 1$ at room temperature. Thermoelastic loss over frequency square $(A/f^2)_{\text{Th}}$ is calculated with the Equation (5). The values of $(A/f^2)_L$, $(A/f^2)_S$, $(A/f^2)_{\text{Th}}$ and total attenuation $(A/f^2)_{\text{Total}}$ are presented in Table 3.

Table 3: Ultrasonic attenuation coefficient (in $10^{-16} \text{ Nps}^2\text{m}^{-1}$) of CrB_2 and MoB_2 compounds.

Alloys	CrB_2	MoB_2
$(A/f^2)_{\text{Th}}$	0.29	0.30
$(A/f^2)_L$	162.66	167.59
$(A/f^2)_S$	39.29	49.87
$(A/f^2)_{\text{Total}}$	202.24	217.76

In the present investigation, the ultrasonic wave propagates along the unique axis of the crystal, the Akhieser type of loss of energy for longitudinal and shear wave and thermo elastic loss increases with the temperature of the material (Table 3). $(A/f^2)_{\text{Akh}}$ is proportional to D , E_0 , τ and V^{-3} (Equations. 4 and 6). The E_0 is increasing and V is decreasing with the temperature (Figs. 1-3). Hence, Akhieser loss in these compounds is predominantly affected by the thermal energy density E_0 and the thermal conductivity.

Therefore, the ultrasonic attenuation increases due to the reduction in the thermal conductivity. Thus ultrasonic attenuation is mainly governed by the phonon–phonon interaction mechanism. A comparison of the ultrasonic attenuation could not be made due to lack of experimental data in the literature.

Table 3 indicate that the thermoelastic loss is very small in comparison to Akhieser loss and ultrasonic attenuation for longitudinal wave $(A/f^2)_L$ is greater than that

of shear wave $(A/f^2)_S$. This reveals that ultrasonic attenuation due to phonon-phonon interaction along longitudinal wave is governing factor for total attenuation $((A/f^2)_{\text{Total}} = (A/f^2)_{\text{Th}} + (A/f^2)_L + (A/f^2)_S)$. The total attenuation is mainly affected by thermal energy density and thermal conductivity. Thus it may predict that at room temperature CrB_2 behaves as its purest form and is more ductile as evinced by minimum attenuation comparison than MoB_2 .

Since $A \propto V^{-3}$ and velocity is the largest for CrB_2 among MoB_2 thus the attenuation A should be smallest and material should be most ductile. The minimum ultrasonic attenuation for CrB_2 justifies its quite stable hcp structure state. The total attenuation of these metals are much larger than other diborides compounds (TiB_2 and OsB_2) due to their large thermal conductivity and acoustic coupling constants [16, 17]. This implies that the interaction between acoustical phonon and quanta of lattice vibration for these metals is large in comparison to third group nitrides.

4. CONCLUSIONS

- Present method to evaluate second and third order elastic constants involving much body interaction potential for hexagonal structured diborides compounds is correct.
- All elastic constants and density are mainly the affecting factor for anomalous behaviour of ultrasonic velocity in these compounds.
- The order of thermal relaxation time for these compounds is found in picoseconds, which justifies their hexagonal structure. The re-establishment time for the equilibrium distribution of thermal phonons will be minimum for the wave propagation along $\theta = 55^\circ$ due to being smallest value of τ along this direction..
- The acoustic coupling constant of these group compounds for longitudinal wave are found larger than other group diborides. Hence the conversion of acoustic energy into thermal energy will be large for these compounds.
- The ultrasonic attenuation due to phonon-phonon interaction mechanism is predominant over total attenuation as a governing factor thermal conductivity.
- The mechanical properties (yield strength, ductility, elastic properties) of CrB_2 are better than MoB_2 , because at low temperature it has high SOEC, ultrasonic velocity and low ultrasonic attenuation.

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